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(54) Title: METHOD OF REDUCING THE EMISSION OF FORMALDEHYDE FROM FORMALDEHYDE LADEN LAYERED PRODUCTS

(57) Abstract: A method of reducing the emission of formaldehyde from formaldehyde laden layered products having at least 2 layers, at least one of which being a veneer, wherein prior to bonding the layers together, at least one side surface of said veneer is treated with a solution comprising an ammonium salt. The invention also relates to a veneer and a flooring material obtainable by the method.

METHOD OF REDUCING THE EMISSION OF FORMALDEHYDE FROM FORMALDEHYDE LADEN LAYERED PRODUCTS

The present invention relates to a method of reducing the emission of formaldehyde from formaldehyde laden layered products, having at least two layers, at least one of which being a veneer. It also relates to a veneer and a flooring material obtainable by the method. The method according to the present invention comprises treatment, prior to bonding the layers together, of at least one of the surfaces of said veneer with a solution comprising an ammonium salt.

Aldehydes, especially formaldehyde based resins, are widely used in adhesive compositions, which are used in the manufacture of construction materials such as panelling, decking, etc.; home furnishings such as furniture, flooring material, etc. Typically, these adhesives compositions contain a substantial molar excess of formaldehyde. Some of this excess formaldehyde is released upon curing of the resin during the manufacture of the product. However, it is well known that formaldehyde continues to be released from these products even after the manufacturing process is completed. Thus, formaldehyde in the indoor air has been a major concern for many years.

Several attempts have been made for many years for reducing formaldehyde emission, but all entail significant mechanical, chemical, environmental or economical disadvantages.

EP 0 144 985 discloses a method of reducing the emission of formaldehyde from chipboards and fibreboards, which fall into emission class E1, veneered with finishing layers. The finishing layer is bonded to the board by using a urea formaldehyde resin as a binder. The boards are treated prior to veneering with an aqueous solution of urea and/or other compounds giving off ammonia.

Moreover, layered flooring material, such as three-layer parquet floor can emit formaldehyde due to the different wood layers being normally bonded together by gluing with formaldehyde based adhesives. The top layer usually consists of hardwood, the middle layer of softwood or a board, for example, MDF (Medium Density Fibre)-board, HDF (High Density Fibre)-board or particle board and the bottom layer of a veneer. The top layer is usually treated with a formaldehyde free UV-lacquer or an oil to protect the surface, which also functions as a barrier to the formaldehyde emission. The different parts of a parquet sample, such as the front, the back, and the edges, give different emission rates. For example, the formaldehyde emission from the backside can be 20 times higher than that from the front side.

Furthermore, there is an increasing demand for parquet flooring which can meet the required E1 value obtained in a chamber test according to the Swedish standard SS 270236 (SS 1988). In cases where the emission test for parquet flooring has been performed with samples having unexposed backsides and sealed edges, the obtained  
5 emission values have been very low, often under  $0.05 \text{ mg/m}^3$  (the limit value for E1 being  $0.13 \text{ mg/m}^3$ ).

Additionally, there is proposed a new European standard, EN 717-1, for formaldehyde emission determination, according to which all samples to be measured will have exposed backside and partially exposed edges. This makes it more difficult for the  
10 flooring producers to achieve extremely low formaldehyde emission values.

Furthermore, there will be demands on meeting the Japanese standard JAS SIS20, which involves a desiccator measurement where the backside and the edges of the sample cannot be sealed, but they are totally exposed.

Thus, technical solutions are still sought for the need to decrease the emission of  
15 formaldehyde from wood-based products containing formaldehyde-based resins, meeting the new more strict standards for formaldehyde emission from these products.

Accordingly, the present invention provides a method of reducing the emission of formaldehyde from wood-based products containing formaldehyde based resins, by which the above mentioned problems are overcome. The method, according to the  
20 present invention, also provides for an easier handling and reduces the risk of discoloration of the finished layered product due to the salt used, comparing to methods where treatment with the salt solution takes place subsequent to bonding of the layers together.

The method, according to the invention, comprises treatment of at least one of  
25 the surfaces of a veneer, comprised in a formaldehyde laden layered product having at least two layers, prior to bonding the layers together, with a solution comprising an ammonium salt.

By "formaldehyde laden layered products" is herein meant layered products containing formaldehyde-based resins, wherein the layers are bonded to each other by a  
30 formaldehyde-based adhesive. Furthermore, in case one or more of the layers in the layered product is a board, e.g., as a middle layer in a flooring material, the board as such may also be bonded with a formaldehyde-based adhesive.

Suitably, the concentration of the ammonium salt in the solution is from about 1 to about 60 weight %, preferably from about 5 to about 40 weight %, and most preferably  
35 from about 8 to about 30 weight %. Moreover, the concentration of the salt in the solution depends on which salt is used, since the water-solubility of different salts may vary and thus different amounts of salt are needed in order to obtain an solution that is effective to

formaldehyde emission. Thus, when the ammonium salt used is an ammonium sulphite, the concentration of it in the solution is suitably from about 1 to about 30 weight %, preferably from about 5 to about 20 weight %, and most preferably from about 8 to about 13 weight %. When the ammonium salt used is an ammonium carbonate, the concentration of it in the solution is suitably from about 5 to about 60 weight %, preferably from about 15 to about 40 weight %, and most preferably from about 20 to about 30 weight %.

Although application of the salt in the form of a solution is preferred, according to the invention, it may also be applied in the form of a powder, if so desired. For environmental reasons, the solution is suitably an aqueous solution, although other solvents than water may be used. The salt solution may be applied by using any conventional coating technique, such as roller coating, curtain coating, or, spray coating. The amount of salt solution applied, when only one of the surfaces is treated, is suitably from about 30 to about 90 g/m<sup>2</sup>, preferably from about 40 to about 80 g/m<sup>2</sup>, and most preferably from about 55 to about 65 g/m<sup>2</sup>. If both of the surfaces are to be treated, then the applied amount per side is suitably half of the amount if only one of the surfaces would be treated. In order to avoid disturbance of the moisture balance of the treated product large amounts of salt solution are undesirable.

Suitable ammonium salts, according to the invention, include, for example, ammonium sulphite or bisulphite, ammonium carbonate, or, ammonium hydrogen carbonate. Preferably, ammonium sulphite or ammonium carbonate is used.

The method of reducing the amount of formaldehyde liberated by materials and products prepared with formaldehyde based resins is applicable to all formaldehyde based resins, for example, it is applicable to urea-formaldehyde, melamine-formaldehyde, phenol-formaldehyde resins and the like as well as copolymers, blends and mixtures made therefrom.

In a preferred embodiment of the invention, urea is added to the ammonium salt solution. Even though the ammonium salt does alone effectively reduce the emission of formaldehyde, addition of urea in the salt solution improves further the reduction of formaldehyde emission. Suitably, the weight ratio of urea to ammonium salt is from about 1:10 to about 1:1, preferably from about 2:10 to about 8:10, and most preferably from about 3:10 to about 6:10.

The salt solution for use in the method according to the invention is prepared by a process, which comprises mixing of the ammonium salt, the urea and the water in a mixing ratio, which gives the desired concentration of salt and urea in the solution.

In a preferred embodiment of the process according to the present invention, the ammonium salt is in the form of an aqueous solution before mixing with the urea and required additional water for receiving a solution with the desired salt concentration.

In a further preferred embodiment of the process according to the invention, both  
5 the ammonium salt and the urea are in the form of aqueous solutions before mixing with each other for preparing an aqueous solution according to the invention with the desired salt concentration.

The veneer to be treated according to the invention may be any kind of wood veneer, preferably untreated veneer.

10 The veneers may be conditioned after the application of the salt solution to desired moisture content before the bonding stage.

The layers can be bonded by using any of the known conventional techniques, for example, by gluing and pressing.

Preferably, the veneer treated by the method according to the invention  
15 constitutes the backside surface or layer of the layered product. This gives rise to a significant reduction of the emission of formaldehyde from the backside of the layered product.

Furthermore, although only one of the surfaces of the veneer need be coated with the salt solution to achieve the benefits of the invention, depending on the  
20 application method both of the surfaces may be coated if so desired.

The layered product, according to the invention, may be any wood-based layered product. Suitably, it is a flooring material, preferably a parquet flooring, and most preferably a three-layer parquet flooring.

The invention is further illustrated by means of the following non-limiting  
25 examples. Parts and percentages relate to parts by weight respectively percent by weight, unless otherwise stated.

#### Examples

The ammonium sulphite solution used in examples 1-8 was prepared by mixing  
30 19.7 kg of ammonium sulphite solution (35-36 weight %) and 3.0 kg urea with water to obtain a 10 weight % aqueous salt solution.

The ammonium carbonate solution used in examples 1-8 was prepared by mixing 31.6 kg urea, 40.0 kg ammonium bicarbonate and 28.4 kg ammonium carbonate with water to obtain a 27.8 weight % aqueous salt solution.

Example 1 (reference): Veneers of spruce (2 mm thick) were glued on both sides  
35 of the core material of pine with a urea-formaldehyde resin and a hardener.

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Example 2: Veneers of spruce (2 mm thick) were pre-treated with an ammonium carbonate solution, on both sides and then left to dry for 4 hours before gluing and pressing in the same way as in example 1.

Example 3 (comparison): The procedure in example 1 was repeated, except that, after gluing and pressing, the sample was left 15 minutes at ambient temperature and then the backside (the side facing away from the glue line) of the veneers was sprayed with an ammonium carbonate solution.

Example 4: Veneers of spruce (2 mm thick) were pre-treated with an ammonium sulphite solution, on both sides, left to dry and then glued and pressed in the same way as in example 2.

Example 5 (comparison): The procedure in example 3 was repeated, except that the backside of the veneers was sprayed with an ammonium sulphite solution.

The formaldehyde emission from all samples prepared according to the above examples was measured with a Field and Laboratory Emission Cell (FLEC) after 24 hours conditioning. The results are shown in table 1 below.

Table 1

Example	Treatment of the veneers	Concentration of the salt solution, % by weight	Applied amount salt solution, g/m <sup>2</sup> per treated side	Emission µg/m <sup>2</sup> h after 24 hours
1	Without treatment			733
2	Pre-treated with an ammonium carbonate solution	27,8	31	44
3	Post-treated with an ammonium carbonate solution	27,8	63	105
4	Pre-treated with an ammonium sulphite solution	10	29	<10
5	Post-treated with an ammonium sulphite solution	10	58	45

As can be seen from table 1, the formaldehyde emission was lower when the veneers were pre-treated than when they were post-treated.

In the following examples 6-8, a 3-layer parquet flooring, 365 mm in length and 260 mm in breadth, was manufactured by bonding the layers together with a urea-formaldehyde resin and a hardener.

Example 6 (reference): A parquet flooring was manufactured using an untreated veneer as a backside layer.

Example 7: A parquet flooring was manufactured using as a backside layer a veneer treated on one side, the side that constitutes the backside surface of the parquet flooring, with an ammonium carbonate solution, before bonding.

Example 8: A parquet flooring was manufactured as in example 1, except that after gluing and pressing the layers together the backside surface of the parquet flooring was treated with an ammonium carbonate solution.

Samples with a size of 250 mm X 250 mm were sawn from the parquet floorings manufactured as above and the formaldehyde emission from the backside was measured with a Field and Laboratory Emission Cell (FLEC) after 24 hours conditioning. The results are shown in table 2 below.

Table 2

Example	Treatment of the veneers	Concentration of the salt solution, % by weight	Applied amount salt solution, g/m <sup>2</sup> per treated side	Emission µg/m <sup>2</sup> h after 24 hours
6	Without treatment			233
7	Pre-treated with an ammonium carbonate solution	27,8	74	30
8	Post-treated with an ammonium carbonate solution	27,8	74	36

Evidently, pre-treatment not only provides for an easier handling during application of the salt solution and eliminates the risk of discolouring the outer layer of the layered product, but it also results in a lower formaldehyde emission.

In the following examples 9-11, an aqueous ammonium sulphite solution of 10 weight % was used, without any urea added.

Example 9 (reference): A laminated structure was manufactured by gluing veneers of beech (0.6 mm thick) on both sides of a core material of plywood with a urea-formaldehyde resin and a hardener.

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Example 10: A laminated structure was manufactured in the same way as in example 9 except that the surfaces on both sides of the core material was pre-treated with an ammonium sulphite solution, and then left to dry for 4 hours before gluing the veneers onto it.

- 5 Example 11: A laminated structure was manufactured in the same way as in example 9 except that the veneers were pre-treated on one side with an ammonium sulphite solution, and then left to dry for 4 hours before gluing.

10 Two samples with a size of 25 mm X 25 mm were sawn from each of the laminated structures of examples 9-11 and the formaldehyde emission was determined by a modified "Flask method" (EN 717-3). Each pair of samples was suspended in 50 ml water at 40°C for 3 hours. The formaldehyde content in the water was determined photometrically by using acetyl acetone and ammonium acetate which react with formaldehyde. The result is expressed as mg formaldehyde per litre and is shown in table 3 below.

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Table 3

Example	Treatment of veneers or core material	Concentration of salt solution, % by weight	Applied amount salt solution, g/m <sup>2</sup> per treated side	Formaldehyde content in water, mg /l
9	Without treatment			2.9
10	Pre-treatment of core material with an ammonium sulphite solution	10	80	1.2
11	Pre-treatment of veneers with an ammonium sulphite solution	10	80	<0.5

As can be seen from table 3, the formaldehyde content was significantly lower when the veneers were pre-treated than when the core material was pre-treated.

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CLAIMS

1. A method of reducing the emission of formaldehyde from formaldehyde laden layered products having at least 2 layers, at least one of which being a veneer, wherein prior to bonding the layers together, at least one of the surfaces of said veneer is treated  
5 with a solution comprising an ammonium salt.
2. A method according to claim 1, wherein said solution is an aqueous solution.
3. A method according to any one of claims 1 or 2, wherein said solution has an ammonium salt content in the range of from about 5 % to about 30 % by weight.
4. A method according to any one of claims 1-3, wherein the ammonium salt is  
10 ammonium sulphite or bisulphite.
5. A method according to any one of claims 1-3, wherein the ammonium salt is ammonium carbonate or ammonium hydrogen carbonate.
6. A method according to any one of claims 1-5, wherein the solution further comprises urea.
7. A method according to claim 6, wherein the weight ratio of urea to ammonium  
15 salt is from about 3:10 to about 6:10.
8. A method according to any one of the preceding claims, wherein the veneer treated by the method according to any one of claims 1-7 constitutes the backside surface or layer of the layered product.
9. A method according to any one of claims 1-8, wherein the layered product is a  
20 flooring material.
10. A method according to claim 9, wherein said flooring material is a parquet flooring.
11. A veneer obtainable by the method according to any one of claims 1-9.
12. A flooring material obtainable by the method according to any one of claims  
25 1-9.
13. A flooring material according to claim 12, wherein said material is a parquet flooring.

# INTERNATIONAL SEARCH REPORT

International Application No.

SE 02/00378

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B27N1/00

According to International Patent Classification (IPC) or to both national classification and IPC

## **B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B27N B27D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## **C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 144 985 A (FRAUNHOFER GES FORSCHUNG) 19 June 1985 (1985-06-19) abstract page 4, line 8 - line 17 page 6, line 1 - line 20; claims ---	1-13
X	DATABASE WPI Section Ch, Week 197407 Derwent Publications Ltd., London, GB; Class A21, AN 1974-12177V XP002171075 & JP 48 072308 A (IMARI GOHAN CO LTD), 29 September 1973 (1973-09-29) abstract --- -/-	1,2

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 198726 Derwent Publications Ltd., London, GB; Class A21, AN 1987-183056 XP002171076 &amp; JP 62 114629 A (MITSUI TOATSU CHEM INC), 26 May 1987 (1987-05-26) abstract</p> <p>---</p>	1-13
A	<p>EP 0 012 169 A (FRAUNHOFER GES FORSCHUNG) 25 June 1980 (1980-06-25)</p> <p>---</p>	
A	<p>GB 2 274 084 A (DENLO PRECISION ENGINEERING LI) 13 July 1994 (1994-07-13)</p> <p>---</p>	
A	<p>US 4 478 966 A (HELGESSION GOETE ET AL) 23 October 1984 (1984-10-23)</p> <p>---</p>	
A	<p>EP 0 006 486 A (SWEDSPAN AB) 9 January 1980 (1980-01-09)</p> <p>---</p>	
A	<p>DATABASE WPI Section Ch, Week 199943 Derwent Publications Ltd., London, GB; Class A17, AN 1999-512835 XP002171077 &amp; JP 11 223023 A (DAIKEN KOGYO KK), 17 August 1999 (1999-08-17) abstract</p> <p>-----</p>	

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/SE 02/00378

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0144985	A	19-06-1985	DE 3344239 A1 AT 93444 T DE 3486202 D1 EP 0144985 A2	01-08-1985 15-09-1993 30-09-1993 19-06-1985
JP 48072308	A	29-09-1973	JP 814851 C JP 50028484 B	14-05-1976 16-09-1975
JP 62114629	A	26-05-1987	NONE	
EP 0012169	A	25-06-1980	DE 2851589 A1 AT 6608 T DE 2966797 D1 EP 0012169 A1	04-06-1980 15-03-1984 19-04-1984 25-06-1980
GB 2274084	A	13-07-1994	BE 1005655 A6	07-12-1993
US 4478966	A	23-10-1984	AT 368766 B AT 315379 A BE 875929 A1 CA 1145499 A1 CH 637063 A5 CS 236760 B2 DD 144083 A5 DE 2917159 A1 DK 165479 A FI 791156 A ,B, FR 2454901 A1 GB 2019854 A ,B IT 1116459 B NL 7903074 A NO 791439 A ,B, PL 215140 A1 SE 409090 B US 4528309 A	10-11-1982 15-03-1982 29-10-1979 26-04-1983 15-07-1983 15-05-1985 24-09-1980 08-11-1979 29-10-1979 29-10-1979 21-11-1980 07-11-1979 10-02-1986 30-10-1979 30-10-1979 11-02-1980 30-07-1979 09-07-1985
EP 0006486	A	09-01-1980	DE 2829021 B1 AT 5823 T DE 2966525 D1 EP 0006486 A2	03-01-1980 15-01-1984 16-02-1984 09-01-1980
JP 11223023	A	17-08-1999	NONE	